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Communications

Facilitated $d\pi-p\pi^*$ Transition in a Novel Organoboron π -Conjugated Polymer Including a Ruthenium–Phosphine Complex

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Summary: A facilitated $d\pi-p\pi^*$ transition was observed in a boron–ruthenium conjugated system prepared by hydroboration polymerization between mesitylborane and a ruthenium–phosphine complex containing tetrayne. In the UV–vis absorption spectrum of the obtained polymer, the absorption maximum of the MLCT band ($d\pi-p\pi^*$ transition) was highly bathochromically shifted by 141 nm relative to that of the tetrayne monomer.

Organometallic polymers composed of transition-metal complexes with alkynyl ligands have been studied extensively, because of their nonlinear optical, liquid crystalline, semiconducting behavior. Although a number of papers on the synthesis of these polymers have been published,¹ the incorporation of the transition

metal in the conjugated backbone with alkynyl linkages normally does not lead to significant activation of the $d\pi-p\pi^*$ transition compared with the monomeric complex, due to the energy mismatch between the metal d-orbitals and alkynyl π^* -orbitals.

To develop effective light-harvesting systems or photo-refractive (PR) materials with sensitized $d\pi-p\pi^*$ transitions, one attractive approach has been synthesis of conjugated polymers with ionic transition metals to form good metal-to-ligand charge-transfer chromophores. Despite the importance of the field, a limited number of papers on such materials have been published.²

On the other hand, we have recently developed a new method for the preparation of novel n-type organoboron conjugated polymers by “hydroboration polymerization”.³ The polymers produced by simple polyaddition between mesitylborane and aromatic diynes exhibit

(1) For example: (a) Takahashi, S.; Kariya, M.; Yatake, T.; Sonogashira, K.; Hagihara, N. *Macromolecules* **1978**, *11*, 1063. (b) Takahashi, S.; Murata, E.; Kariya, M.; Sonogashira, K.; Hagihara, N. *Macromolecules* **1979**, *12*, 1016. (c) Onitsuka, K.; Ogawa, H.; Jho, T.; Takahashi, S. *Chem. Lett.* **1988**, 1855. (d) Fyfe, H. B.; Mlekuz, M.; Zargarian, D.; Taylor, N. J.; Marder, T. B. *J. Chem. Soc., Chem. Commun.* **1991**, 188. (e) Khan, M. S.; Kakkar, A. K.; Ingham, S. L.; Raithby, P. R.; Lewis, J.; Spencer, B.; Whittman, F.; Friend, R. H. *J. Organomet. Chem.* **1994**, *472*, 247. (f) Lavastre, O.; Even, M.; Pacreau, A.; Vairon, J. P.; Dixneuf, P. H. *Organometallics* **1996**, *15*, 1530.

(2) For example: (a) Yamamoto, T.; Maruyama, T.; Zhou, Z.; Ito, T.; Fukuda, T.; Yoneda, Y.; Begum, F.; Ikeda, T.; Sasaki, S.; Takezoe, H.; Fukuda, A.; Kubota, K. *J. Am. Chem. Soc.* **1994**, *116*, 4832. (b) Peng, Z.; Yu, L. *J. Am. Chem. Soc.* **1996**, *118*, 3777. (c) Ley, K. D.; Whittle, C. E.; Bartberger, M. D.; Schanze, K. S. *J. Am. Chem. Soc.* **1997**, *119*, 3423.

(3) Matsumi, N.; Naka, K.; Chujo, Y. *J. Am. Chem. Soc.* **1998**, *120*, 5112.

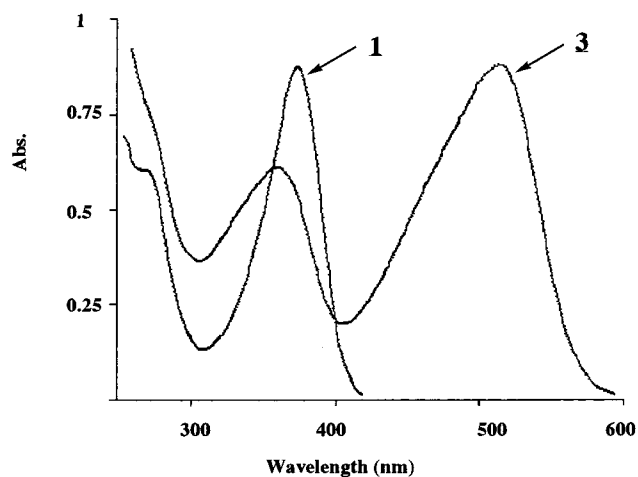


Figure 1. UV-vis absorption spectra of **1** and **3** in chloroform at room temperature.

their absorption maxima in a visible region owing to expansion of π -conjugation path via the empty p-orbital of the boron atom. If these systems are introduced in rigid-rod polymers, the organoboron conjugated channel with high electron affinity might facilitate the $d\pi$ - $p\pi^*$ transition process in rigid-rod polymers, because the $d\pi$ - $p\pi^*$ transition is equal to n-type doping for the backbone, in which dissociated electrons are injected. Importantly, in this system, a $d\pi$ - $p\pi^*$ transition can be activated *in the direction of the conjugated backbone*, which might enable the preparation of novel types of narrow band gap polymers.⁴

Furthermore, hydroboration polymerization proceeds smoothly without any catalyst under fairly mild reaction conditions and no side product is formed throughout the reaction. Therefore, the obtained polymer can be quite easily purified by washing with a poor solvent without using acidic solution or chelating agents. This would enable an incorporation of a wide variety of organometallic complexes in the conjugated backbone.

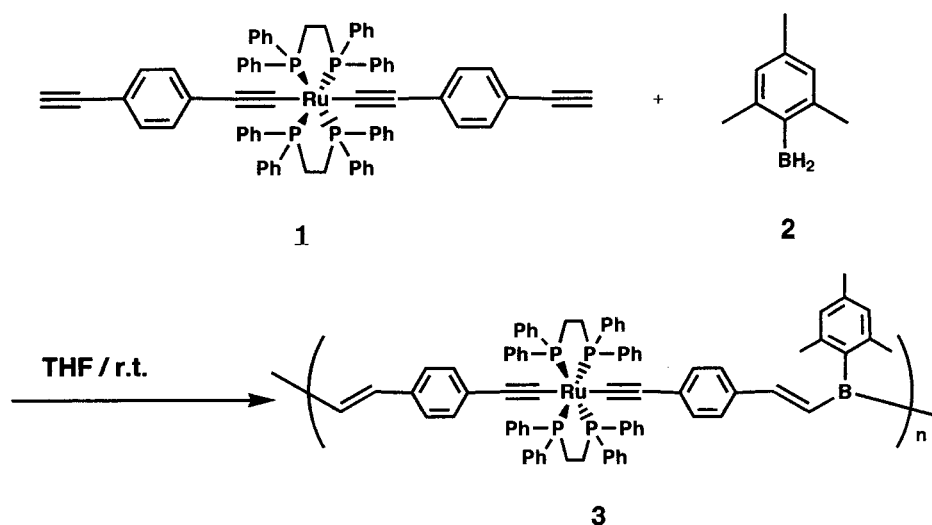
We report herein the synthesis of a novel organoboron conjugated polymer including a ruthenium-phosphine complex by means of a hydroboration polymerization of a ruthenium-containing tetrayne monomer (Scheme 1). The obtained polymer showed a bathochromically shifted $d\pi$ - $p\pi^*$ transition in its UV-vis spectrum (Figure 1).

Hydroboration polymerization between mesitylborane⁵ and Ru-monomer^{1f} was carried out as follows. To a suspension of Ru-monomer in freshly distilled THF, an excess amount of mesitylborane in THF (MesBH₂/Ru-monomer = 1.17) was added dropwise at room temperature. During the addition, the heterogeneous reaction mixture turned to a homogeneous red solution. After the mixture was stirred for 5 h, evaporation of the solvent gave a red gum, which was purified by washing with methanol repeatedly to give a red powder in 91% yield. The obtained polymer was highly soluble in common organic solvents such as THF, chloroform, and benzene, despite its relatively rigid structure. In a semiempirical calculation of the conformation of the polymer prepared from 1,4-diethynylbenzene,⁶ it was indicated that the direction of mesityl group was almost perpendicular to the main chain. This conformation and also the steric hindrance induced by the bulky dppe ligands might retard the interchain stacking effectively. The gel permeation chromatographic analysis (GPC; THF as an eluent, PSt standards) of the polymer showed a unimodal peak, in which the number-average molecular weight and the polydispersity were found to be 13 000 and 1.8, respectively.

The structure of the polymer was supported by IR and ¹H, ¹¹B, and ³¹P NMR spectra. The IR spectrum showed two strong absorptions at 1578 and 2053 cm⁻¹ due to the stretching of the double bond and the ruthenium acetylide triple bond, respectively. In the ¹H NMR spectrum, peaks assignable to the mesityl group were observed at 2.19 and 6.71 ppm, and a peak at 2.65 ppm was assigned to the CH₂CH₂ bridge of dppe ligands. All the peaks were in good agreement with those for the expected structure. The ¹¹B NMR spectrum of the polymer showed the main peak at 2.26 ppm. This is shifted to higher field in comparison with the typical chemical shift of dialkenylborane (around 30 ppm) and indicates a relatively electron rich environment of the boron atom. In the ³¹P NMR spectrum, only one peak was observed at 55.8 ppm, characteristic of an octahedral geometry of the ruthenium center with a trans arrangement of the two acetylide functions. This indicates that the structure of the ruthenium complex was not affected under the polymerization conditions.

The electrochemical behavior of the monomer and

Scheme 1



polymer was studied by cyclic voltammetry. The monomer showed a single reversible oxidation wave (Ru^{III}/Ru^{II}, $E^\circ = 0.45$ V vs SCE ($i_{p,a}/i_{p,c} = 1.02$),⁷ and the polymer showed a similar electrochemical response at significantly higher potential (Ru^{III}/Ru^{II}, $E^\circ = 0.56$ V vs SCE ($i_{p,a}/i_{p,c} = 0.98$), indicating a slight decrease of the electronic density of the ruthenium atom.

The UV-vis absorption spectrum of the polymer showed two absorption maxima at 359 and 514 nm, possibly due to $\pi-\pi^*$ and $d\pi-p\pi^*$ transitions in the main chain, respectively (Figure 1). The former indicates

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(5) Smith, K.; Pelter, A.; Jin, Z. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 851.

(6) Calculated by a self-consistent-field crystal-orbital method: Matsumi, N.; Chujo, Y.; Okada, M.; Tanaka, K. To be submitted for publication.

(7) Lavastre, O.; Plass, J.; Bachmann, P.; Guesmi, S.; Moinet, C.; Dixneuf, P. H. *Organometallics* **1997**, *16*, 184.

extended π -conjugation length through the boron atom. The latter is unusually bathochromically shifted by 141 nm in comparison with that of Ru-monomer (Figure 1). It is hard to explain this phenomenon only in terms of the extension of π -conjugation. As described before, the high electron affinity of the organoboron unit and the push-pull effect between the electron-rich ruthenium complex and the electron-deficient organoboron unit might be responsible for this red shift.

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Supporting Information Available: Text giving experimental details and figures giving NMR, IR, and fluorescence emission spectra for **3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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